

On the Origins of Sudden Adhesion Loss at a Critical Relative Humidity: Examination of Bulk and Interfacial Contributions

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The origins for abrupt adhesion loss at a critical relative humidity (RH) for polymeric adhesives bonded to inorganic surfaces have been explored using a model poly(methyl methacrylate) (PMMA) film on glass. The interfacial and bulk water concentrations within the polymer film as a function of D₂O partial pressure were quantified using neutron reflectivity. Adhesion strength of these PMMA/SiO₂ interfaces under the same conditions was quantified using a shaft loaded blister test. A drop in adhesion strength was observed at a critical RH, and at this same RH, a discontinuity in the bulk moisture concentration occurred. The moisture concentration near the interface was higher than that in the bulk PMMA, and at the critical RH, the breadth of the interfacial water concentration distribution as a function of distance from the SiO₂/PMMA interface increased dramatically. We propose a mechanism for loss of adhesion at a critical RH based upon the interplay between bulk swelling induced stress and weakening of the interfacial bond by moisture accumulation at the PMMA/SiO₂ interface.

Introduction

Adhesion loss due to environmental factors has been a fundamental problem within the adhesive's industry.^{1–5} A main cause of adhesion loss is ambient moisture. Many adhesives exhibit catastrophic failure when the environment exceeds a critical relative humidity (RH).^{6–10} The mechanisms of adhesion loss at high RH is still a topic of current research. It is generally agreed that physical and chemical changes resulting from moisture absorption by the adhesive cause the loss of adhesion, but the relative roles of the bulk adhesive and the adhesive/substrate interface is still an open question. Brewis et al.⁶ attributed a sudden loss in adhesion in an epoxy/aluminum system to hydration of the metal oxide. More recent work has examined adhesion loss of a single polymer adhered to different surfaces at high and low humidity. This work demonstrated that the adhesive strength above the critical RH is extremely dependent upon the surface chemistry of the substrate.¹¹ In contrast, Lefebvre et al.⁸ proposed that the amount of water in the adhesive is critical, and the quantity

of absorbed water depends on the chemical nature of the adhesive. They proposed that the presence of hydroxyls in the adhesive increases the concentration of absorbed water at a given RH. The increased water within the adhesive would give rise to swelling pressure at the interface. Support for this proposed mechanism of adhesion loss was provided by the observation that there was a discontinuity in the bulk equilibrium moisture sorption curve at the same RH as that producing a drop in adhesion strength.

The contradicting mechanisms proposed by Lefebvre and Brewis for the abrupt adhesion loss at high RH suggest completely different approaches to improving the adhesion of polymeric materials under these conditions. Understanding of the mechanism for adhesive failure at high humidity is critical for the development of rational strategies to improve performance and increase confidence in the use of adhesives where these conditions are encountered. In this letter, we seek to elucidate the fundamental mechanisms of adhesion loss at a critical RH by combining detailed characterization of the moisture distribution within the film using neutron reflectivity (NR) and measurement of the adhesive strength using a fracture mechanics approach. A change in the interfacial characteristics that corresponds with the discontinuity in the bulk sorption near the critical RH is shown. A combined bulk–interfacial mechanism for adhesion loss is proposed.

Experimental Details

Materials. Atactic poly(methyl methacrylate) (PMMA) ($M_n = 1.2 \times 10^5$ g/mol, $T_g = 108$ °C) was used as the model adhesive. Films of PMMA were prepared by spin coating from a toluene solution. Two different substrates for the films were prepared: silicon wafers with a thermal oxide layer for NR, and borosilicate glass with an 8 mm diameter hole for adhesive strength measurements due to experimental requirements of the two measurements. The thermal oxide layer is necessary to accurately resolve the interfacial concentrations at low RH, while the poor mechanical properties of silicon necessitates mechanical reinforcement for use in the shaft loaded blister test (SLBT) for adhesion. However, both surfaces are predominately SiO_x; the surface chemistry is known to affect both

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[†] Building and Fire Research Laboratory, NIST.

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^{||} Arizona State University.

(1) Kinloch, A. J. *Adhesion and Adhesives: Science and Technology*; Chapman and Hall: London, 1987.

(2) Kinloch, A. J.; Korenberg, C. F.; Tan, K. T.; Watts, J. F. *J. Mater. Sci.* **2007**, *42*, 6353.

(3) White, C. C.; Tan, K. T.; O'Brien, E. P.; Hunston, D. L. *Proceedings of the 29th Annual Meeting of the Adhesion Society*; Anderson, G., Ed.; Adhesion Society, Inc.: Blacksburg, VA, 2006; p 353.

(4) Nguyen, T.; Byrd, E.; Bentz, D.; Lin, C. *Prog. Org. Coat.* **1996**, *27*, 181.

(5) Venables, J. D. *J. Mater. Sci.* **1984**, *19*, 2431.

(6) Brewis, D. M.; Comyn, J.; Raval, A. K.; Kinloch, A. J. *Int. J. Adhes. Adhes.* **1990**, *10*, 247.

(7) Cognard, J. *Int. J. Adhes. Adhes.* **1988**, *8*, 93.

(8) Lefebvre, D. R.; Takahashi, K. M.; Muller, A. J.; Raju, V. R. *J. Adhes. Sci. Technol.* **1991**, *5*, 201.

(9) Comyn, J.; Groves, C.; Saville, R. *Int. J. Adhes. Adhes.* **1994**, *14*, 15.

(10) Gledhill, R. A.; Kinloch, A. J. *J. Adhes.* **1974**, *6*, 315.

(11) O'Brien, E. P.; White, C. C.; Vogt, B. D. *Adv. Eng. Mater.* **2006**, *8*, 114.

the interfacial moisture and adhesion.¹¹ The similar surfaces should result in negligible difference between the two substrates for properties of interest in this work (adhesion and interfacial moisture content). All substrates were rigorously cleaned with acetone prior to use.

Adhesive Joint Preparation. For the measurement of adhesive strength, multilayered specimens were prepared. The precrack was formed by covering the hole in the glass substrate with Kapton¹² pressure-sensitive adhesive tape (PSAT). A nominal 15 μm thick PMMA film was then spin-coated over the glass and Kapton PSAT. A top laminate, which served as a mechanical reinforcing layer, consisted of a Kapton E film bonded to the PMMA using a bisphenol A resin cured with 43 phr Jeffamine T-403. The composite adhesive layer was cured at room temperature for 48 h and then at 60 $^{\circ}\text{C}$ for 1 h.

Environmental Preconditioning. The joints were preconditioned within a Tenney temperature humidity chamber at a constant RH of 2, 25, 42.5, 50, 60, 62.5, 65.1, 68.5, 70, 85, or 100% $\pm 2\%$ for 3 days at room temperature, (23.0 ± 0.2) $^{\circ}\text{C}$. For each exposure, the water uptake reached equilibrium prior to testing. After environmental exposure, the joints were immediately tested at ambient conditions (nominally 23 $^{\circ}\text{C}$ and 25% RH).

Fracture Mechanics Measurements. The joint strengths were characterized with shaft loaded blister experiments using an Instron tensile testing machine at a cross-head displacement rate of 0.005 mm/s. The adhesive fracture energy, G_C , was calculated from the load-based equation:^{13,14}

$$G_C = \left(\frac{1}{16\pi^4 E h} \right)^{\frac{1}{3}} \cdot \left(\frac{P}{a} \right)^{\frac{4}{3}} \quad (1)$$

where P is the load, a is the crack length, E is the Young's modulus, and h is the total thickness of the composite layer. The modulus of the composite layer was estimated from the rule of mixtures.¹⁴ Three joints were tested at each RH.

Water Sorption Isotherms in Bulk PMMA. The water sorption isotherm measurement was performed in a Hiden *IGAsorp* moisture sorption analyzer at (23.0 ± 0.1) $^{\circ}\text{C}$. The Hiden *IGAsorp* has a microbalance having a mass resolution of 0.1 μg and can accurately control the environmental chamber to within $\pm 0.5\%$ RH. Specimens consisted of square PMMA slabs (5 mm \times 5 mm \times 0.25 mm). Replicate measurements indicated that the isotherm data were reproducible.

Neutron Reflectivity. NR measurements were performed on the NG-7 reflectometer at the Center for Neutron Research at the National Institute of Standards and Technology (Gaithersburg, MD) in the following configuration: wavelength (λ) = 4.768 \AA and wavelength spread ($\Delta\lambda/\lambda$) = 0.025. NR is capable of probing the neutron scattering density at depths of up to several thousand angstroms, with an effective depth resolution of several angstroms. Deuterium oxide (Aldrich, 99.9% pure) was utilized to enable direct quantification of the water distribution within the film. The environment surrounding the PMMA film was controlled during the neutron measurements by using a humidity generator with D_2O and nitrogen as the carrier gas and flowing this stream through an aluminum vessel equipped with two quartz windows. The RH is directly related to the partial pressure of the water through normalization with the saturation vapor pressure at the temperature of interest. However, deuteration leads to a shift in the saturation pressure of water due to isotopic effects; therefore the quantity of water available in the vapor phase at identical RH is different between H_2O and D_2O . For clarity, the moisture content in the vapor phase is reported as the partial pressure for the D_2O to avoid ambiguities between H_2O and D_2O .

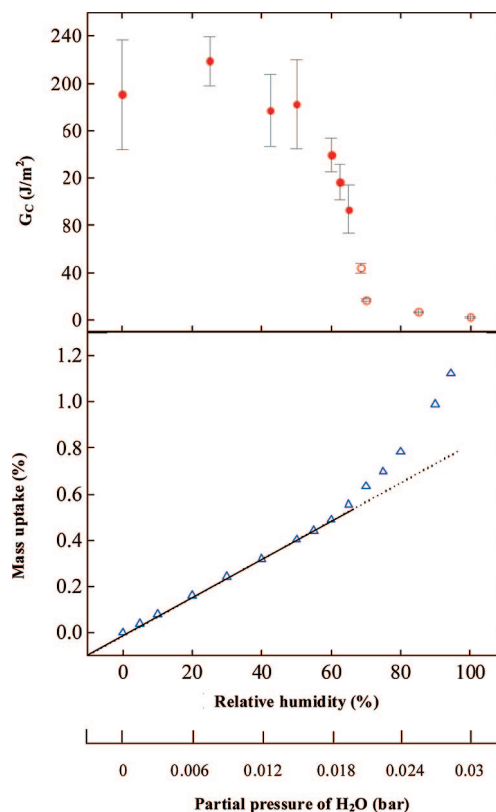


Figure 1. (a) Strength of the PMMA on glass joint as a function of RH. A precipitous drop in G_C near 65% RH is indicative of the critical RH. The solid symbols indicate cohesive or partially cohesive failure, while the open symbols indicate a fully adhesive failure of the joint. The error bars represent $\pm 1\sigma$ from the mean value. (b) Moisture uptake in bulk PMMA samples. Note that a deviation from Henry's law prediction (solid line) occurs at the critical RH for adhesion.

Results and Discussion

The critical RH for adhesion of PMMA to glass was determined using the SLBT. The relationship between G_C and RH from SLBT measurements is shown in Figure 1a. At low humidity levels (<50% RH), the joint had good adhesion, as demonstrated by the relatively high G_C values, which are insensitive to RH. Failure of the joints occurs via cohesive crack growth within the PMMA layer in a stick-slip manner. Thus, failure at low humidity is controlled by the cohesive strength of the PMMA. For RH between 60% and 68%, the stick-slip crack growth behavior during failure of the joint was observed; however, G_C values decreased by nearly 2 orders of magnitude. Above 60% RH, a complex failure path involving both cohesive failure within the PMMA layer and truly interfacial failure along the PMMA/oxide interface (as determined by X-ray photoelectron spectroscopy) was observed. The extreme sensitivity of G_C to RH is an indication of the presence of a critical RH for adhesion. At higher humidities (>68% RH), stable crack growth (as opposed to stick-slip) was observed at low values of G_C . For all measurements of joint failure where the sample was conditioned at a humidity >68%, X-ray photoelectron spectroscopy indicates the fracture occurred at the PMMA/oxide interface with no appreciable PMMA remaining on the glass. For samples conditioned at these high RH values, the failure mechanism for the PMMA/oxide joints changed from cohesive failure to adhesive failure with a transition regime of mixed cohesive and adhesive failure near the critical RH.

Measurements of the equilibrium water sorption isotherm for bulk PMMA are shown in Figure 1b. A linear increase (Henry's

(12) Certain commercial products or equipment are described in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that it is necessarily the best available for the purpose.

(13) Wan, K. T.; Mai, Y. W. *Int. J. Fract. Mech.* **1995**, *74*, 181.

(14) O'Brien, E. P.; Ward, T. C.; Guo, S.; Dillard, D. A. *J. Adhes.* **2003**, *79*, 69.

Law) in the water concentration with respect to RH is observed up to the critical RH (Figure 1a). Above this RH value, a positive deviation from linearity (Henry's law) was found. Similar to prior reports,^{8,15} the deviation in the bulk moisture solubility occurs near the critical RH where abrupt adhesion loss was observed. This observation is consistent with the postulation that the critical RH effect is strongly influenced by the bulk adhesive properties.^{8,15} The bulk swelling of adhesive materials is commonly used to assess the moisture solubility in adhesive coatings.

However, a number of observations are inconsistent with this hypothesis. First, the failure mechanism for the joints shifts from cohesive to adhesive at the critical RH; it is cohesive failure where the bulk mechanical properties of the polymer are dominant, while adhesive failure is a result of the poor interfacial strength of the joint. Thus, an interfacial phenomenon would be expected to be the root cause of the precipitous decrease in the adhesive strength, not a bulk effect. Additionally, work by O'Brien et al. on adhesion of PMMA on substrates with different surface pretreatments demonstrated that the surface chemistry can be used as a tool to control the decrease in adhesive joint strength upon exposure to saturated water vapor.¹¹ Values of G_C were measured for samples in a dry state and under exposure to 100% RH. For a highly hydrophobic surface (treated with *n*-octyl-trichlorosilane, $\theta_{\text{water}} = 95^\circ$), the G_C values were the same for both conditions with interfacial failure. With a clean glass surface (i.e., highly hydrophilic), G_C dropped by several orders of magnitude when going from dry to wet conditions with a shift from cohesive to interfacial failure. The wet measurements are well above the critical RH but are consistent with the existence of a sudden loss in adhesion at some intermediate RH value. Since bulk moisture absorption is independent of the surface chemistry, the critical RH effect can not be attributed solely to the amount of water absorbed.

Despite these observations, the critical RH for adhesion loss occurs at the same humidity level as a deviation in the equilibrium bulk moisture solubility. This phenomenon raises the question of how the water concentration near the interface relates to the bulk water concentration. A direct proportionality between the two might be expected; however, NR measurements of D_2O saturated polymer films have demonstrated that the interfacial concentration is independent of the bulk concentration¹⁶ and dependent upon the surface chemistry.¹⁷ Thus, for understanding the origins of adhesion loss at the critical RH, the moisture distribution at the joint interface as the humidity passes through the critical RH is an important question.

NR was utilized to quantify the distribution of moisture near the PMMA/oxide interface as a function of D_2O partial pressure. The reflectivity profiles are fit recursively using a series of slabs of fixed scattering length density in the Parratt formalism.¹⁸ Previously, for moisture accumulation at a polymer/ Al_2O_3 interface, the D_2O accumulation at the interface manifests itself as an apparent increase in the oxide layer, which decreases the uncertainty in the concentration profile.¹⁴ For this study, a nominally 15 nm thick thermal oxide layer is utilized to provide this improvement in uncertainty for SiO_2 . The real-space D_2O concentration profiles through the film are calculated from the change in the scattering length density profiles between the dry

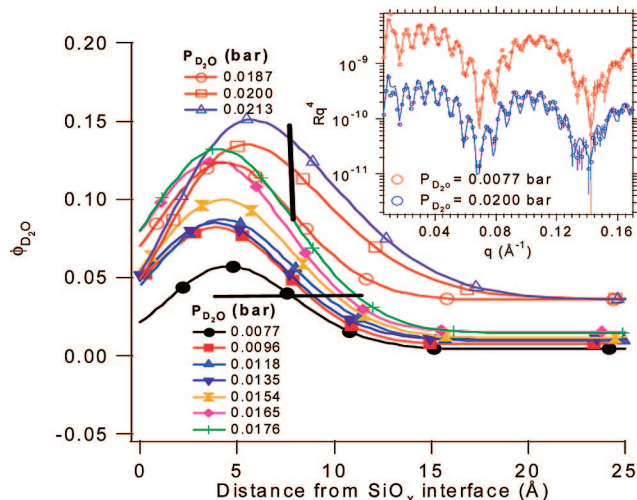


Figure 2. Water concentration profiles near the PMMA/silicon oxide interface at various partial pressures of D_2O as determined from NR. The inset graph shows the NR data and associated fitting line plotted as Rq^4 versus q for the P_{D_2O} of 0.0077 bar, and P_{D_2O} of 0.0200 bar.

and wet states. There are three components whose concentration must be determined. First, the concentration of the SiO_2 (from the finite roughness of the interface) as a function of distance into the PMMA film was determined for the dry state as follows:

$$\phi_{SiO_2}(x) = \frac{Q_c^2(x) - Q_{c,PMMA}^2}{Q_{c,SiO_2}^2 - Q_{c,PMMA}^2} \quad (2)$$

where $Q_c^2(x)$ is the scattering length density at position x in the film, Q_{c,SiO_2}^2 is the scattering length density of the pure SiO_2 and $Q_{c,PMMA}^2$ is the scattering length density of pure PMMA. With the assumption that the SiO_2 is immobile and impervious to D_2O , the water concentration profile is calculated as

$$\phi_w(x) = \frac{Q_c^2(x) - (1 - \phi_{SiO_2}(x))Q_{c,PMMA}^2 - \phi_{SiO_2}(x) \cdot Q_{c,SiO_2}^2}{Q_{c,D_2O}^2 - Q_{c,PMMA}^2} \quad (3)$$

where $\phi_w(x)$ is the water concentration at position x in the film, and Q_{c,D_2O}^2 is the scattering length density for pure D_2O . Figure 2 shows the calculated D_2O concentration profiles as a function of distance from the interface for various RHs. For a given RH, an increase in the concentration of moisture at the interfacial region in comparison to the bulk solubility is observed. This accumulation layer peaks within about 5 Å of the silicon oxide surface. Such accumulation of water at the interface is expected as the silicon oxide is more hydrophilic, i.e., has a stronger affinity for water, than the bulk polymer. The lower concentration that is very near the silicon oxide interface is attributed to intrinsic roughness of the oxide layer, leading to a dilution of the PMMA/water phase. This result is consistent with prior measurements of Al_2O_3 sputtered surfaces that have a finite roughness; the interfacial moisture concentration for polymers on this surface also goes through a maximum.¹⁷ Additionally, thermal oxide typically has been shown to not grow by a strictly layer-by-layer mechanism, thus a rough surface is expected.¹⁹

Examination of Figure 2 shows that the amount of moisture both at the interface and in the bulk polymer generally increases as the humidity increases. There is a noticeable jump in the bulk concentration as the D_2O pressure is increased beyond 0.018

(15) Lefebvre, D. R.; Elliker, K. M.; Takahashi, K. M.; Raju, V. R.; Kaplan, M. L. *J. Adhes. Sci. Technol.* **2000**, *14*, 925.

(16) Vogt, B. D.; Soles, C. L.; Jones, R. L.; Wang, C.-Y.; Lin, E. K.; Wu, W.-I.; Satija, S. K. *Langmuir* **2004**, *20*, 5285.

(17) Vogt, B. D.; Prabhu, V. M.; Soles, C. L.; Satija, S. K.; Lin, E. K.; Wu, W.-I. *Langmuir* **2005**, *21*, 2460.

(18) Parratt, L. G. *Phys. Rev.* **1954**, *95*, 359.

(19) Hojo, D.; Tokuda, N.; Yamabe, K. *Thin Solid Films* **2007**, *515*, 7892.

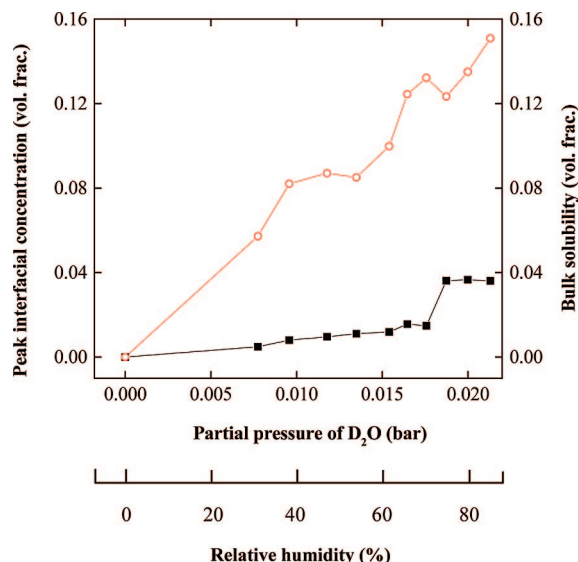


Figure 3. Comparison of interfacial and bulk D_2O concentrations determined using NR. A significant excess is observed at the interface (O) that increases approximately linearly with humidity. The bulk solubility of D_2O in PMMA (■) shows a discontinuity near the critical RH. The lines in the figure are guides for the eye.

bar; this corresponds to the RH range where both the deviation in bulk concentration in the sorption curve and the loss of adhesion strength are observed. The bulk concentration measured from NR agrees qualitatively with the gravimetric measurements of bulk samples, but there appears to be enhanced solubility in the thin film. This difference is not simply an isotopic substitution effect, as H_2O sorption into PMMA films measured using a quartz crystal microbalance agrees well with the neutron data. Interestingly, a recent report on the moisture uptake into polymer films has only reported the sorption for RH less than 60% into PMMA, but higher humidities are reported for other polymers.²⁰ Figure 2 suggests that the maximum in D_2O concentration at the interface is not the root of the adhesive failure at the critical RH, as there is no change in the interfacial excess maximum concentration between 0.0176 and 0.0187 bar. The total excess D_2O is more difficult to directly visualize. This excess corresponds to the integral of the D_2O concentration profile less the bulk concentration. A comparison of the bulk concentration and total interfacial excess is shown in Figure 3. As the D_2O partial pressure is increased beyond 0.018 bar, there is a obvious jump in the bulk moisture concentration for the films. This jump corresponds to the same humidity where the bulk sorption deviates from Henry's law. However, the concentration of moisture near the interface does not show any discontinuity; rather it increases linearly with partial pressure, even through the critical RH. The lack of a discontinuity in the interfacial moisture concentration near the critical RH is surprising, as the joint failure occurred along the PMMA/oxide interface at or above the critical RH.

Invoking a thermodynamic argument as the interfacial moisture content increases, the interface should be appreciably weakened.^{1,2} It can then be suggested that the root cause for the adhesion loss at the critical RH was the result of two factors: the physical changes induced in the bulk from moisture absorption, and a weakening of the interface caused by the large concentration of accumulated moisture. Unlike a number of other adhesive systems, however, the PMMA/oxide interface is still stable when moisture is present. This combined with the very low fracture energies

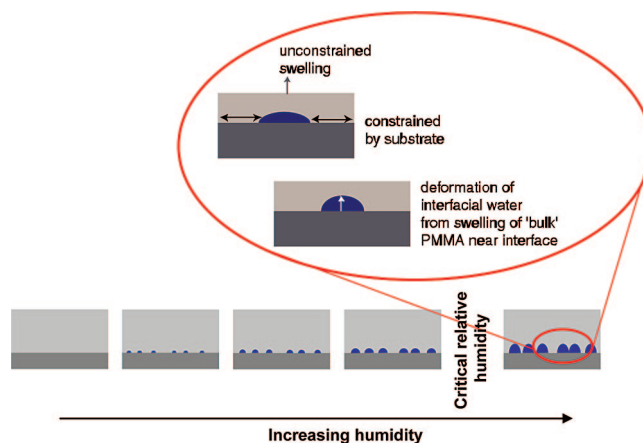


Figure 4. Schematic diagram of the proposed mechanism of adhesion failure at the critical RH based upon coupled interfacial and bulk swelling effects. The water phase at the interface grows as the humidity is increased; this decreases the contact area between the polymer and substrate (glass). The increase in bulk solubility at the critical RH leads to significant swelling. The interfacial water is then compressed, but the difference in constraint between in-plane and out-of-plane expansion results in deformation of the water phase, leading to a normal force that decreases the energy requirement for adhesive failure.

measured above the critical RH suggests that another factor may also contribute to the critical loss of adhesion. Moreover, the thermodynamic argument does not address why there is a sudden drop in fracture resistance over a very small range of humidities. One additional factor that has been mentioned is swelling-induced stresses.^{21,22} During water sorption, a polymer, such as PMMA, expands in response to the stresses induced by the osmotic pressure leading to swelling.^{23–25} In a film geometry, the constraint of the substrate causes stresses to develop. Quantifying these stresses is difficult since they depend on the materials, previous processing, and time.^{21,22,26} Moreover, higher concentration of water near the interface would complicate the analysis. For a full adhesive bond, partial sorption of moisture by the adhesive during early stages near the edge leads to swelling, inducing compressive stresses near the edges and large tensile stresses in the center. Once saturation is achieved, the elimination of the swelling gradient and the relaxation of the polymer reduce the compressive and tensile stresses, but tensile stresses now concentrate in the vicinity of edges. In the present study, an equilibrated condition was reached for each specimen prior to testing, so the most likely situation is for localized tensile stresses at the edges. Since the measurements here involve measuring the energy required to propagate a crack, it is quite possible that the swelling-generated stresses contribute to the crack tip stress field and reduce the external load that needs to be applied to propagate the crack.

On the basis of these ideas, a mechanism such as that illustrated schematically in Figure 4 might be suggested. At low RHs, the interfacial strength is higher than the cohesive strength of the bulk polymer, so the joint failure occurred entirely cohesively within the bulk polymer. At higher humidity, moisture sorption (up to 3% volume fraction at high RH) produces swelling stresses, but this alone is not sufficient to cause the drop in fracture energy, since changing to a moderately hydrophobic interface ($\theta_{\text{water}} =$

(21) Weitsman, J. J. *Composite Mater.* **1977**, 11, 378.

(22) Lam, D. C. C.; Yang, F.; Tong, P. *IEEE Trans. Compon. Packag. Manuf. Technol.* **1999**, 22, 215.

(23) Souder, W.; Paffenbarger, G. C. *Physical Properties of Dental Materials*; Circular No. C433; National Bureau of Standards: Washington, DC, 1942.

(24) Pekcan, O.; Ugur, S.; Yilmaz, Y. *Polymer* **1997**, 38, 2183.

(25) Turner, D. T. *Polymer* **1982**, 23, 197.

(26) Weitsman, J. *Int. J. Solids Struct.* **1979**, 15, 701.

(20) Manoli, K.; Goustouridis, D.; Chatzandroulis, S.; Raptis, I.; Valamontes, E. S.; Sanopoulou, M. *Polymer* **2006**, 47, 6117.

78°) eliminates the sudden drop in fracture energy at the critical RH. In addition to any contribution for swelling stresses to weaken the interface, moisture also attacks the interface itself. At high RH values, the concentration of water at the interface is greater than the solubility limit in PMMA, so phase separation occurs at the interface;²⁷ the exact nature of this phase separation is not known, as only information through the film is obtained from NR. Evidence of this phase separation is provided as Supporting Information. As the moisture content at the interface is increased, the effective contact area of the polymer with the substrate is reduced, hence weakening the interface. Since a water phase is not capable of transferring any stress, the forces from bulk swelling would be further concentrated in bonded areas of the interface. This proposed coupled bulk–interface mechanism is consistent with experimental observations near the critical RH.

Further examination of the D₂O concentration profiles (Figure 2) illustrates a change in the interfacial moisture concentration profiles above the critical RH that is also consistent with the proposed coupled bulk–interface mechanism. Figure 5 shows the full width at half-peak maximum (fwhm) of the interfacial water concentration as a function of partial pressure. The fwhm of the interfacial water concentration increases significantly above the critical RH and can be explained by stresses near the interface that increase the moisture content in the PMMA. Below the critical RH, the fwhm of the interfacial moisture concentration is nearly invariant, but it increases sharply at partial pressures above the critical RH. Analogous to stress corrosion cracking phenomena,²⁸ water uptake at the PMMA/oxide interface could also be enhanced by the swelling stresses. The interface, therefore, is further weakened by the presence of more water molecules, and the failure now occurs via failure of these broader discrete domains of water molecules near the interface. In summary, the interplay between bulk polymer swelling and the interface appears to be the critical factor in the adhesion loss at the critical RH.

Conclusions

NR and adhesive strength measurements made using fracture mechanics were combined to elucidate the fundamental origins

(27) Vogt, B. D.; Soles, C. L.; Wang, C.-Y.; Prabhu, V. M.; McGuiggan, P. M.; Douglas, J. F.; Lin, E. K.; Wu, W.-I.; Satija, S. K.; Goldfard, D. L.; Angelopoulos, M. J. *Microolithogr., Microfabr., Microsyst.* **2005**, *4*, 013003.

(28) *Stress Corrosion Cracking*; Yahalom, J., Aladjem, A., Eds.; Freund: Tel-Aviv, 1980.

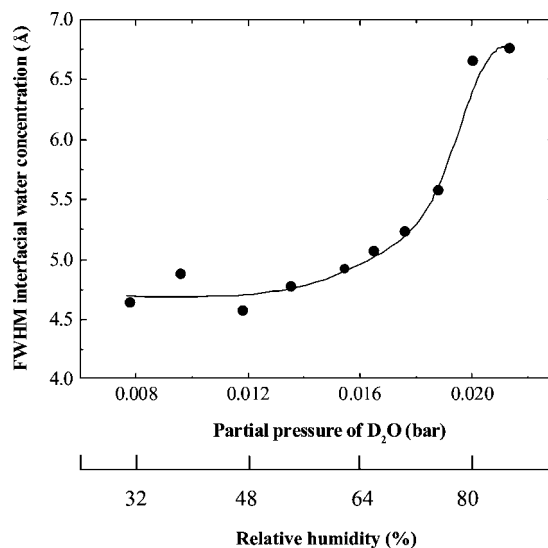


Figure 5. The fwhm of the interfacial D₂O concentration excess as a function of the humidity. The fwhm is nearly constant below the critical RH and then increases significantly above the critical RH.

of the adhesion loss at a critical RH for a model system of PMMA on glass. Discontinuities in the adhesive strength, bulk moisture solubility, and the width of the interfacial moisture excess were observed at the critical RH. A mechanism for loss of adhesion at the critical RH is proposed on the basis of a coupling of bulk swelling-induced stresses and decreased interfacial strength due to moisture accumulation at the PMMA/glass oxide interface.

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Supporting Information Available: Images suggesting the phase separation of water at the buried interface are included. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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